

**IN THE UNITED STATES  
PATENT AND TRADEMARK OFFICE**

**TITLE:**

Polymer Manufacturing Process

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## **BACKGROUND OF THE INVENTION**

### **1. Field of The Invention**

Applicant's invention relates to a polymer manufacturing process that utilizes polyethylene terephthalate.

### **2. Background Information**

Esterification is the condensation of organic carboxylic acids and alcohols to yield ester linkages. Polyesters are made when multifunctional carboxylic acids are reacted with multifunctional alcohols to yield polymers containing repeating ester units. Polyesters have become important polymer components used in a variety of industries.

The esterification reaction required to manufacture polyester polymers takes a great deal of time compared to other polymerization reactions. For example a typical aromatic polyester of moderate molecular weight can require between 12 and 24 hours to finish whereas an aromatic styrene polymer prepared by free radical polymerization can take as little as one hour to complete. There are several reasons for this increased duration. One reason is that the temperatures required for esterification are much higher on the order of 200 to 250 degrees Centigrade than those of other reactions such as free radical polymerization which require temperatures of only 70 to 100 degrees Centigrade. Another reason more time is needed is when higher molecular weight polyesters (such as those greater than 10,000 average number mw) are the goal. With higher molecular weight polyesters

1 when the equivalents of hydroxyl and acid components are closer to being equal, the  
2 reaction becomes longer. While initially the reaction proceeds rapidly at first, once  
3 reaction temperatures have been reached the reaction starts slowing down as the  
4 free acids and hydroxyl groups become less concentrated in the mix. As the reaction  
5 slows additional steps and techniques are used to continue the reaction and create  
6 larger and larger molecular weights. With very large molecular weights (those  
7 greater than 30,000 mw) most often the material is transferred from the original  
8 vessel to one where more surface area, heat and/or agitation can be applied. Even  
9 larger molecular weights can be obtained by using additional processing steps such  
10 as solid state reactions or transesterification.

11 The following is an excerpt from Organic Chemistry by Morrison and Boyd,  
12 pages 679-680 , second edition: "In the esterification of an acid, an alcohol acts as  
13 a nucleophilic reagent; in hydrolysis of an ester, an alcohol is displaced by a  
14 nucleophilic reagent. Knowing this, we are not surprised to find that one alcohol is  
15 capable of displacing another alcohol from an ester. This alcoholysis (cleavage by  
16 an alcohol) of an ester is called transesterification." "Transesterification is an  
17 equilibrium reaction. To shift the equilibrium to the right, it is necessary to use a  
18 large excess of the alcohol whose ester we wish to make, or else to remove one of  
19 the products from the reaction mixture. The second approach is the better one  
20 when feasible, since in this way the reaction can be driven to completion."

21 When making condensation polyesters, transesterification can be used as an

1 additional processing step to achieve higher molecular weights with already  
2 condensed polymers or monomers. At higher temperatures the elimination of an  
3 alcohol and subsequent removal of it by vacuum will greatly increase molecular  
4 weight. At some point the end group can be liberated and removed by heat and/or  
5 vacuum thus building molecular weight. To extend the molecular weight of  
6 preformed polymers, transesterification sometimes follows an initial esterification  
7 step where the monomer mix, usually containing excess glycols, is first reacted to a  
8 point where most of the free carboxylic groups are used up. Or transesterification  
9 can be used alone to create polymers where the carboxylic groups have been pre-  
10 formed into esters with an easily volatilized alcohol, most commonly methanol.  
11 Thus both esterification and transesterification can be used separately or together in  
12 the process of making polyesters.

13 Over the years, many processes have been developed for manufacturing  
14 polyesters. In the 1940's it was discovered that polyester polymers could be made  
15 having very desirable properties such as clarity and high impact strength through the  
16 condensation of aromatic dicarboxylic acids with glycols using high temperatures  
17 and long reaction times to achieve higher molecular weights. By far the most  
18 important synthetic polyester today is polyethylene terephthalate (PET). This  
19 polymer is one where the multifunctional carboxylic acid is a terephthalate or  
20 terephthalic acid and the multifunctional alcohol is ethylene glycol. PET is a  
21 crystalline polymer that can be used for a variety of items such as film textile, fiber,

1 beverage bottles, and other types of containers.

2       One method of making PET is to start with dimethyl terephthalate and  
3 transesterify with ethylene glycol liberating methanol. As methanol is removed from  
4 the process the molecular weight is driven up. Several transesterification catalysts  
5 have been used for this method. Due to the environmental problems associated with  
6 methanol, it has become more common to use terephthalic acid and ethylene glycol  
7 with a suitable esterification catalyst. Again there are a number of such catalysts  
8 used.

9       Esterification of terephthalic acid requires high temperatures, in excess of  
10 200 degrees Centigrade, and long reaction times, sometimes longer than 24 hours.

11       Thus it becomes a very energy intensive polymer to make. When very high  
12 molecular weights are needed, 50,000 or greater (which is considered low  
13 compared to other polymers), solid state reactors are used to vacuum as much  
14 glycol off as possible thus extending the chain length through transesterification and  
15 the removal of glycol. Additional heat and time are needed.

16       The PET manufacturing segment of the polymer industry has become so large  
17 that the cost of the raw materials of the PET polymer is low in comparison to other  
18 similar performance polymers. Large PET processing lines dedicated entirely to the  
19 manufacture of the PET polymers produce PET polymer on a continuous basis. Due  
20 to this production there has been a great deal of controversy over the large amounts  
21 of PET that are being recovered from post consumer waste streams. Due to this

1 abundance of post consumer waste, there have been a large number of patents  
2 issued that concern the utilization of this PET waste. As we progress in the  
3 manufacturing techniques for other monomers and the need for higher performance  
4 materials become greater we will naturally expect to see the utilization of other  
5 condensation polymers to the point where they become prevalent in the waste  
6 streams. This has already started to happen with PET containing other barrier  
7 materials and with PEN or polyethylene naphthalate.

8       As the waste stream from recycling started producing waste PET in  
9 abundance there were several patents written to utilize this potential raw material  
10 source. These patents became a technology in their own right. The first approaches  
11 to using PET were geared toward breaking down the ester linkages through  
12 hydrolysis with water or glycolysis. Glycolysis is a specific form of transesterification  
13 where excess glycol is used to degrade the molecular weight. In this way the  
14 individual components of the PET can be regenerated. In U.S. Patent 4,078,143  
15 issued to Malik, et al. entitled "Process for depolymerizing waste ethylene  
16 terephthalate polyester", a process is described where PET is broken down by  
17 glycolysis to bis-(2-hydroxy ethyl) terephthalate, a monomer that can be utilized to  
18 reform the PET. In U.S. Patent 4,163,860, issued to Delatte, et al. entitled  
19 "Process for obtaining dimethyl terephthalate from polyester scrap" methanol is used  
20 to transesterify scrap PET back to dimethyl terephthalate that is purified for use in  
21 the PET manufacturing process. In U.S. Patent 4,355,175, issued to Pasztaszeri

1 entitled "Method for recovery to terephthalic acid from polyester scrap", a method of  
2 hydrolyzing the PET and purifying and recovering the terephthalic acid is described.

3 In U.S. Patent 4,578,502 issued to Cudmore entitled "Polyethylene terephthalate  
4 saponification process", a process is described wherein PET is broken down into its  
5 monomeric constituents through saponification with alkali. In U.S. Patent  
6 4,929,749 issued to Gupta, et al. entitled "Production of terephthalate esters by  
7 degradative transesterification of scrap or virgin terephthalate polyesters", higher  
8 boiling alcohols are used to transesterify the PET into lower molecular weight  
9 materials for use as raw materials for the manufacture of other polymers. In US  
10 Patent 5,101,064 issued to Dupont, et al. entitled "Production of terephthalate  
11 esters by degradative transesterification of scrap or virgin terephthalate polyesters",  
12 a process is described where groups having 6-20 carbons are used to degrade the  
13 PET, distill off the glycol byproduct, and recover the diester.

14 In US Patent 5,266,601 issued to Kyber, et al. entitled "Process for  
15 preparing polybutylene terephthalate from PET scrap" a method of using PET by  
16 glycolysis and ester exchange with 1,4 butanediol and subsequent polycondensation  
17 is described. In US Patent 5,319,128 issued to Dupont, et al. entitled "Production  
18 of terephthalate esters by degradative transesterification of scrap or virgin  
19 terephthalate polyesters" a method of transesterifying PET using higher molecular  
20 weight alcohols with 6 to 20 carbons and then recovering the diesters of  
21 terephthalate is described. In US Patent 6,031,128 and 6,075,163 issued to Roh,

1 et al. entitled "Process for manufacturing terephthalic acid", a process is described  
2 for manufacturing terephthalic acid from waste PET whereby PET is hydrolyzed to  
3 disodium terephthalate and then acid neutralized to recover the free terephthalic  
4 acid. In US Patent 6,472,557 issued to Pell, Jr. et al. entitled "Process for  
5 recycling polyesters", a process for depolymerizing PET to dimethylterephthalate and  
6 then hydrolyzing it to terephthalic acid for reuse is described. Although all of these  
7 processes work, they are all very energy intensive ways of recycling the PET and do  
8 not utilize the time and energy that has already gone into making the PET polyester.  
9 More often these processes end up costing as much or even more than the cost of  
10 the monomers they are trying to reclaim. This is in large part due to the low cost of  
11 the beginning PET feed stocks and the refined methods for converting to the starting  
12 monomers. Also the additional energy required to reclaim the monomers from  
13 recycled PET adds substantially to the cost.

14 In the techniques used below, it is not necessary to take the PET polymer all  
15 the way to its monomeric constituents and thus at least part of the time and energy  
16 of conversion of the terephthalic acid and ethylene glycol is conserved. However in  
17 all cases the transesterification conversion is done to break down the PET linkages  
18 and lower the molecular weight to much lower oligomeric forms prior to subsequent  
19 reactions.

20 There are also a number of methods for the utilization of PET as a raw  
21 material for the manufacture of other polymers where terephthalic acid and/or



1 ethylene glycol can be integrated as one of the components. One such area is in the  
2 use of PET to make polyols that in turn are used for making urethane foams. In US  
3 Patent 4,439,549 issued to Brennan entitled "Novel aromatic polyester polyol  
4 mixtures made from polyethylene terephthalate residues and alkylene oxides" a  
5 method of reacting PET with glycol to degrade to an oligomeric polyol and then  
6 subsequent reaction of the polyol with an isocyanate moiety to produce rigid foam is  
7 described. In US Patent 4,469,824 issued to Gigsby, Jr., et al. entitled "Liquid  
8 terephthalic ester polyols and polyisocyanate foams therefrom", PET is digested with  
9 diethylene glycol and other glycols with some of the ethylene glycol and then  
10 removed to form a polyol that reacts with an isocyanate to form a polyisocyanate  
11 foam. In US Patent 4,485,196 issued to Speranza in entitled "Liquid phase polyols  
12 which are alkylene oxide adducts of terephthalic esters" a technique of making  
13 polyols for further processing into urethane foams is described. The polyol is further  
14 reacted by ethoxylation or propoxylation to liquefy and inhibit crystallinity. It is then  
15 useful for further conversion into polyurethanes. In US Patent 5,948,828 issued to  
16 Reck entitled "Technology development and consultancy" reclaimed PET is digested  
17 with diethylene glycol, insolubles are removed, and ethylene glycol and free  
18 diethylene glycol are removed to achieve a final hydroxyl value for a polyol. In US  
19 Patent 6,573,304 issued to Durant, et al. in June of 2003 entitled "Method for  
20 obtaining polyols and polyol thus obtained" a process for transesterification with  
21 glycols and subsequent removal of free glycols stopping at a narrow molecular

1 weight is described. These methods utilize excess glycol and transesterification to  
2 shift the equilibrium back to lower molecular weight entities that can be further  
3 processed.

4       Some techniques developed utilizing PET have at least partially preserved  
5 some of the ester moieties and therefore some of the time and energy already used  
6 in making the PET. In U.S. Patent 4,977,191 issued to Salsman entitled "Water-  
7 soluble or water dispersible polyester sizing compositions", a process is described  
8 where other polymers are made by first degrading the PET into oligomers containing  
9 the terephthalate moiety and second building back up the molecular weight using  
10 other aromatic or aliphatic acids. In US Patent 5,726,277 issued to Salsman  
11 entitled "Adhesive compositions from phthalate polymers and the preparation  
12 thereof" adhesive compositions are described that are made from PET that is  
13 digested or transesterified with glycols and oxyalkylated polyols, either ethoxylated  
14 or propoxylated. A similar type of reaction is used in US Patent 5,958,601 issued to  
15 Salsman entitled "Water dispersible/redispersible hydrophobic polyesters resins and  
16 their application in coatings". In this patent however an ester of a fatty acid and  
17 alcohol containing free hydroxyl groups is used in combination with glycols to  
18 degrade the PET polymer to lower molecular weight species before a molecular  
19 weight buildup is done with additional aromatic acids.

20       There are additional polymer applications where PET has been used as a raw  
21 material as well. In US Patent 5,820,982 issued to Salsman entitled "Sulfoaryl

1 modified water-soluble or water-dispersible resins from polyethylene terephthalate or  
2 terephthalates" compositions are described which contain the terephthalate moieties  
3 along with sulfonated aromatic groups. Such resins are useful for adhesives, ink  
4 resins, dye leveling on polyester and nylon fibers, etc. The process for preparation of  
5 these compositions requires a PET glycolysis step followed by additional acids and a  
6 molecular weight buildup esterification step. The processing times can be 12 to 24  
7 hours. In US Patent 6,133,329 issued to Shieh, et al. entitled "Thermoplastic  
8 polyester resin composition" a composition is described where PET is first digested  
9 with a glycol mixture for 3 hours at high temperatures and then reacted with a  
10 natural oil for making it compatible with hydrocarbon and hydrofluorocarbon blowing  
11 agents. In US Patent 6,512,046 issued to Ueno, et al. entitled "Polymerizable  
12 unsaturated polyester resin composition" several compositions are described where  
13 PET is first depolymerized to achieve a polyester skeleton, then built back up with a  
14 dibasic acid, and further reacted with an unsaturated monomer. In US Patent  
15 6,534,624 issued to Ito, et al. entitled "Process for producing alkyd resins" a  
16 process is described where polyester is depolymerized and then esterified in a  
17 mixture of alcohols, glycols, fatty acids, etc. It is noted in this patent that the use of  
18 terephthalic acid has not been in practice in the past with alkyd technology because  
19 this component is more costly than phthalic or phthalic anhydride. Again all of  
20 these patents, some very recent, describe first a depolymerization step and then an  
21 esterification step to build back up molecular weight to make polymers suitable for

1 other areas of use.

2 Other techniques deal with the use of reclaimed PET by cleaning up the PET  
3 from other wastes and using it as a co-blend prior to or in an extruder with virgin  
4 PET or other polymers that can be coextruded with the PET. Once reheated PET  
5 loses intrinsic viscosity (I.V.). Intrinsic viscosity has become a much easier method  
6 of comparing molecular weights of PET than other more time consuming methods.  
7 Once processed, the intrinsic viscosity drops and its use as a feedstock for the  
8 original article made becomes limited. In US Patent 5,225,130 issued to Deiringer  
9 entitled "Process for reclaiming thermally strained polyester scrap material" mixed  
10 streams of recycled PET are cleaned and post condensed with virgin PET. In US  
11 Patent 5,503,790 issued to Clements entitled "Method of producing disposable  
12 articles utilizing regrind polyethylene terephthalate" recycled PET is used to create  
13 articles that are less demanding of higher intrinsic viscosity. In US Patent  
14 5,554,657 issued to Brownscombe, et al. entitled "Process for recycling mixed  
15 polymer containing polyethylene terephthalate" a process for recovering PET that  
16 involves dissolving the PET from a recycled stream, removing the solvents, and  
17 rinsing the PET is described. In US Patent 6,399,695 issued to Moriwaki, et al.  
18 entitled "Thermoplastic polyester resin composition" PET is melted with a polyolefin  
19 or glycidyl methacrylate to produce a composite material. In US Patent 6,583,217  
20 issued to Li, et al. entitled "Composite material composed of fly ash and waste  
21 polyethylene terephthalate" the PET is mixed with the entitled materials and

1 extruded. In the above references no reaction of the PET takes place even though  
2 there are subsequent reprocessing steps. There are many other references where  
3 recycled PET is cleaned and used as part of the mixture back into articles such  
4 bottles, film, etc. Limitations due to the lower intrinsic viscosity of the recycled PET  
5 reduce the amount used in critical applications to 5% or less.

6       There are also current practices where PET is modified by transesterifying  
7 with polyethers. These can be glycols or alcohols that have been ethoxylated or  
8 propoxylated. These polymers contain the block segments of PET with block  
9 segments of the polyethers and thus usually exhibit properties of both. In US Patent  
10 4,785,060 issued to Nagler entitled "Soil release promoting PET-POET copolymer,  
11 method of producing same and use thereof in detergent composition having soil  
12 release promoting property" PET and a polyoxyethylene polymer are reacted together  
13 in a reactor such that an equilibrium is reached. This reaction is based on  
14 transesterification of the hydroxyl end groups of the polyether with the ester linkages  
15 contained in the PET. In US Patent 6,454,982 issued to Branum entitled "Method  
16 of preparing polyethylene modified polyester filaments" a method is described  
17 wherein polyethylene glycol is reacted into PET under transesterification conditions  
18 and solid stated to a higher intrinsic viscosity.

19       In the referenced prior art, glycols, polyethers, or simple glycol monoesters  
20 are used to degrade or lower the molecular weight of the PET in order to get to  
21 monomeric or oligomeric forms of terephthalic acid that can be further utilized as a

1 polyol source for urethanes, to use as adhesive components with glycidyl ethers to  
2 form epoxies, or as coatings and/or adhesives.

3 Another polymer of commerce is polyethylene naphthalate PEN. Within the  
4 last few years there has been much activity in the use of PET with PEN polymers.  
5 This is due in part to better properties such as clarity, strength, and increased  
6 crystallinity that translates to better barrier properties obtained with PEN. However,  
7 PEN is much more expensive than PET. Therefore, several processes for making  
8 copolymers of the two have been developed. In US Patent 5,902,539 issued to  
9 Schmidt, et al. entitled "Process for making PEN/PET blends and transparent  
10 articles therefrom" a process is described where ethylene glycol is used to reduce  
11 the intrinsic viscosity and increase the range of use for PET and PEN copolymers.

12 The following is an excerpt from US Patent 6,414,063, issued to Bassam, et  
13 al. entitled "Nucleated pet/pen polyester compositions".

14 "It is known that medium content PET/PEN compositions (compositions with  
15 PET:PEN ratios around 50:50) are amorphous in nature. The range of  
16 compositions which display this amorphous behaviour is generally accepted  
17 to be around PET:PEN=20:80 to PET:PEN=80:20, as described by two  
18 PEN manufacturers--Shell (see FIG. 1 of presentation to "BevPak" conference,  
19 Spring 1995, USA) and Hoechst-Trevira (page 4 of Polyclear.RTM. N  
20 technical literature). The disadvantage of this behaviour is that the use  
21 temperature of compositions in the 80/20-20/80 region is substantially

1 reduced. The use temperature is dependent on the glass transition  
2 temperature (T<sub>g</sub>) in this region. In contrast, the use temperature of PET/PEN  
3 compositions with <20% PET or <20% PEN is dependent on the crystalline  
4 melt temperature (T<sub>m</sub>). T<sub>m</sub> is over 100.degree. C. higher than the T<sub>g</sub> for  
5 PET/PEN compositions; hence resulting in the substantial reduction in use  
6 temperature observed in the 20/80-80/20 composition region. The same  
7 observations on the amorphous/crystalline nature of PET/PEN compositions  
8 were also made by Lu and Windle (see FIG. 2 in Polymer 36 (1995), pages  
9 451-459) and Andresen and Zachmann (Colloid & Polymer Science 272  
10 (1994), page 1352). Andresen and Zachmann also found that blends of PET  
11 and PEN formed a single phase within 2 minutes of melting. This is usually  
12 good evidence for rapid formation of a PET/PEN copolyester by  
13 transesterification. Thus the behaviour of PET/PEN blends and copolymers  
14 can be expected to be the same with regards to crystallisation during all melt  
15 processing operations. In the case of bottle manufacture using PET/PEN  
16 copolymers and blends, U.S. Pat. No. 5,628,957 (to Continental PET  
17 Technologies Inc.) states that mid-range PET/PEN compositions containing  
18 20-80% PEN are substantially amorphous and describes the use of an  
19 additional strain-hardenable (ie. crystallisable) layer for these mid-range  
20 PET/PEN bottles.”  
21 It is especially interesting to note from this patent that the blends formed a

1 single phase within 2 minutes of melting. Presumably from this and information  
2 presented in the description one can surmise that ester compatibility increases the  
3 rate of transesterification. Also, it can be inferred that PET and PEN copolymer  
4 combinations have been made via melting and/or processing since combinations of  
5 the two polymers were started. Again transesterification of the two is the chemistry  
6 that makes this happen. In US Patent 6,586,558 issued to Schmidt, et al. entitled  
7 "Process for making PEN/PET blends and transparent articles therefrom" glycols are  
8 used to lower the intrinsic viscosity and allow more processable viscosities for  
9 blends of these two polymers. Again transesterification allows this to occur.

10 While there has been a lot of activity directed toward utilizing PET as a raw  
11 material to manufacture other polymers or as a composite material, PET is not being  
12 utilized in these polymers as a raw material. The problems that exist with these  
13 prior techniques include raw material contamination, difficulty of reaction, and  
14 incompatibility with one or more of the other reactive groups. For instance, in US  
15 Patent 5,250,333 issued to McNeely, et al. entitled "Modified polyethylene  
16 terephthalate" there is described compositions where other alkoxylated polyols and  
17 dicarboxylic acids are used in combination with terephthalic acid and ethylene glycol  
18 to produce a less crystalline form of PET. Indeed there are many applications that  
19 use terephthalate moieties but require less crystallinity than that of PET. For  
20 instance, there are many film applications that require less crystallinity for more  
21 elastomeric properties. The polyols mentioned in the previous paragraphs are



1 another example. In US Patent 6,428,900 issued to Wang entitled "Sulfonated  
2 copolyester based water dispersible hot melt adhesive" a polyester which contains  
3 water dispersible sulfonated branched copolyester polymers is described. These  
4 copolyester polymers use difunctional carboxylic acids like terephthalic acid in their  
5 makeup. Crystallinity would inhibit water redispersibility which is an important  
6 aspect of the disclosure. In US Patent 6,555,623 issued to Yang, et al. entitled  
7 "Preparation of unsaturated polyesters" a process is described where MPD (methyl  
8 propanediol) is used along with aromatic diacids such as terephthalic acid and  
9 maleic anhydride to produce unsaturated polyesters suitable for further reaction  
10 through the unsaturated group. Again polymer crystallinity is to be avoided.

11       There are a number of polymers that currently utilize phthalic anhydride as a  
12 preferred difunctional aromatic acid. One reason for this is that for practical  
13 considerations one of the acid groups has already been reacted and is an anhydride.

14       This lowers the weight percent needed in the subsequent polymers being made. In  
15 addition phthalic anhydride esterifies at lower temperatures than terephthalic acid.  
16 Using terephthalic acid as an alternate would not be as economical to begin with.  
17 But terephthalic acid could be used if the right process to use recycled PET were  
18 available that would eliminate this economical difference.

19       There are a number of polymers containing ester linkages and the number  
20 and scope of polymers that utilize or could utilize the raw materials that make up  
21 PET or other condensation polymers of commerce are too numerous to list within

1 the scope of this write. The following broad based articles of commerce all use or  
2 have used terephthalic acid (or aromatic acids like phthalic acid or anhydride)  
3 and/or ethylene glycol in their monomer makeup:

- 4 (1) Adhesives: either hot melt, water borne, or reactive;
- 5 (2) Ink resins: both as the binding agent and the carrier vehicle;
- 6 (3) Unsaturated resins: alone or in combinations with reactive diluents such  
7 as acrylics or styrene for composite mixtures with fiberglass, carbon fiber,  
8 etc.;
- 9 (4) Alkyd resins: both long and short alkyds for coatings and paint  
10 applications;
- 11 (5) Urethanes: As the polyol portion together with isocyanates to form  
12 adhesives, structural resins, or foams;
- 13 (6) Films: Less crystalline films for shrink wrap, laminating, etc.; and
- 14 (7) Polyols for powder coatings or fusable coatings.

15 As seen in the prior art, PET (either virgin or recycled) is recognized as a  
16 material that can be used to make more PET, PET composites, or other polymers  
17 that contain terephthalate groups. The processes that have been used to  
18 accomplish this contain within their steps glycolysis (or hydrolysis) of the ester  
19 linkages to create the beginning monomers such as terephthalic acid, or a much  
20 lower molecular weight terephthalate oligomer that can be reacted to generate more  
21 PET or other polymers through esterification. In no circumstance has there been

1 activity that indicates advantage taken of the high molecular weight of PET  
2 (polyester polymers) being used to build higher molecular weight, on the order of  
3 10,000 to 20,000, through transesterification with a lower molecular weight  
4 polyester.

5 The present process however does. The process of the present invention is a  
6 two-step process that can be used to take full advantage of the high molecular  
7 weight of the precondensed polymer, like PET, itself to produce a high molecular  
8 weight polymer. The first step, which involves no polymer of commerce, takes all  
9 the other monomers that are to be contained within the finished polymer, and reacts  
10 them to form a modifying polymer containing terminal hydroxyl or carboxyl groups.

11 In the second step a commercially available condensation polymer is transesterified  
12 with the modifying polymer using heat and agitation to form the finished polymer.

13 At suitable temperatures as will be herein discussed, the second step occurs very  
14 rapidly (on the order of approximately one-half of the current process) and can be  
15 performed in any vessel such as an extruder set up for reactive extrusion that can be  
16 heated to suitable transesterification temperatures, usually 230 to 270 degrees

17 Centigrade for PET. The advantages of this process are to reduce the manufacturing  
18 time to a time on the order of approximately one-half of the current process and to  
19 produce a higher molecular weight polymer, on the order of greater than 192 g/mol,  
20 which relates to the decreasing time in a decreasing log/log curve of molecular  
21 weight versus time for direct esterification.

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**SUMMARY OF THE INVENTION**

It is an object of the present invention to provide a novel process for manufacturing a polymer.

Still another object of the present invention is to provide a novel process for manufacturing a polymer from PET or PEN.

An additional object of the present invention is to provide a novel process for modifying PET or PEN.

Yet another object of the present invention is to provide a novel process for modifying PET or PEN without degradation to form a higher molecular weight polymer.

It is an additional object of the present invention to provide a novel process for modifying PET or PEN by synthesizing a modifying polymer from a plurality of appropriate monomers.

Still an additional object of the present invention is to provide a novel process for modifying PET or PEN by transesterifying the modifying polymer with the PET or PEN.

In satisfaction of these and related objectives, Applicant's present invention provides a process for manufacturing a polymer from PET or PEN. The process involves modifying PET or PEN without degradation by first synthesizing a modifying polymer from a plurality of appropriate monomers and second transesterifying the modifying polymer with the PET or PEN to form a higher molecular weight polymer.

## **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

The term "modifying polymer" for purposes of this patent is defined as a polymer, not necessarily a polyester polymer, used to modify through transesterification a PET, PEN, or other polymer of commerce to achieve a new polymer with new desired properties.

In the process disclosed herein two steps are used. The first step is the manufacture of a modifying polymer containing the desired ingredients not derived from the commercially available condensation polymer itself. This differs substantially from the other techniques described that utilize PET in that the first step itself does not involve the PET or the monomers that make up PET. This first step of the reaction of the present invention to achieve a modifying polymer reduces the condensation or esterification reactions to only those that are different from the condensation polymer of the second step thereby having lower energy requirements and lower toxic waste stream condensation products. Also, where less crystalline aromatic polymers are desired, the condensation of other aromatic acids to form the modifying polymer is much less energy consumptive than the condensation of terephthalic acid as in the case of PET. In addition, if the goal is to produce a polyol or alkyd, then the modifying polymer reaction proceeds extremely rapidly on the order of a few hours due to the excess of hydroxyl components to acid components. This is in itself a much more rapid condensation than a polymer whose carboxyl and hydroxyl functions are more closely equal, which could take more than 24 hours.

1 Where aliphatic acids for the polymer constituents are used at a temperature range  
2 from 150 to 250 degrees Centigrade, the reaction is further shortened due to the  
3 higher reaction rates, sometimes double that of aromatics. With the use of  
4 terephthalic acid at a temperature of 190 to 270 degrees Centigrade, a reasonable  
5 reaction rate can also be obtained.

6 The second step of the present process is the rapid transesterification of a  
7 commercially available condensation polymer with the modifying polymer produced  
8 in the first step. Careful monitoring of temperatures and reaction rates are not  
9 necessary with the only requirement being enough heat to transesterify the two  
10 polymers in a given length of time because if heating is a problem, the reaction time  
11 can be increased. Higher temperatures will greatly reduce the time required.

12 Reaction rates are dependent on several factors including (1) time, (2) temperature,  
13 (3) modifying polymer molecular weight, (4) hydrophilicity of modifying polymer,  
14 (5) number and type of hydroxyl functionality on modifying polymer, and (6)  
15 transesterification catalyst. Therefore, good transesterification of terephthalates  
16 starts around 200 degrees Centigrade, greatly accelerates around 240 degrees  
17 Centigrade, and is very rapid around 260 degrees Centigrade. Reaction time at 200  
18 degrees Centigrade is about ten hours to transesterify PET with a glycol. Reaction  
19 rate is reduced to about one hour at 240 degrees Centigrade and only fifteen  
20 minutes at 260 degrees Centigrade. In an extruder, heating is not an issue so one  
21 can heat to 300 degrees Centigrade and transesterify even quicker. With a more

1 hydrophobic modifying polymer and secondary hydroxyl groups, these times would  
2 be longer. Thus, a rapid reaction rate can be achieved in the first step if the  
3 modifying polymer is lower molecular weight than the commercially available  
4 condensation polymer or if it contains monomers whose reaction temperatures are  
5 lower than that of the condensation polymer. In this regard it becomes easier to  
6 consider the transesterification step as the molecular weight building step for the  
7 lower molecular weight polymers. Even if the objective is higher molecular weights  
8 it is still far easier to esterify a smaller batch given the charging, heat up cycles, etc.  
9 than any of the current processes or techniques currently utilizing condensation  
10 polymers of commerce such as PET.

11 Transesterification is a reaction that takes place when a group such as an  
12 alcohol or amine becomes a nucleophile and exchanges take places at the ester  
13 linkage. This group can come from any molecule and is not limited to a simple  
14 molecule such as a carbon chained alcohol with 6 to 12 carbons, a glycol with 6 to  
15 20 carbon atoms or an amine with 2 to 20 carbon atoms. Indeed a polymer  
16 containing these groups can be made to react by first transesterifying ester groups  
17 contained on a premanufactured polyester such as PET or PEN. However, since  
18 transesterification continuously occurs above the polymers Tg (glass transition  
19 temperature), the alcohol generated from the nucleophile displacement itself  
20 becomes a nucleophile that can further react. In this way at some point equilibrium  
21 is reached where no further change in the polymer mixture occurs and the mixture

1 becomes a homogeneous new polymer. If the mixture contains polymer segments  
2 that for some reason do not participate in the transesterification reactions, then the  
3 new polymer becomes a copolymer of the two beginning polymers. If the mixture  
4 contains segments that participate more or less equally in the tranesterification  
5 process, then the product becomes more or less a homogeneous polymer with  
6 completely new properties.

7         One of the parameters important to control in polymer synthesis is molecular  
8 weight. With the manufacture of esters, the molecular build up is rapid initially and  
9 slows down considerably as the molecular weight increases. With the present  
10 process the final molecular weight is controlled by the molecular weight of the  
11 modifying polymer and the percentage of that modifying polymer reacted with the  
12 commercially available condensation polymer. For instance, if PET is used as the  
13 commercially available condensation polymer and its quantity is held constant, then  
14 the molecular weight of the finished polymer is solely dependent on the molecular  
15 weight of the modifying polymer. In this way polymers of lower molecular weight  
16 than the commercially available condensation polymer, especially in the range of  
17 less than 15,000, become extremely quick to manufacture compared to other  
18 techniques (approximately one-half the time as other techniques).

19         The second step of the present process can be done in the same  
20 manufacturing vessel or any suitable closed vessel separate from the vessel used to  
21 manufacture the modifying polymer. In some instances the second step does not



1 require the condensers or condensation receivers that are required in the first step  
2 and so less expensive equipment can be used. In fact it is possible to do the second  
3 step in an extruder set up for the needed dwell times and agitation required.

4       If no condensate is removed from the second step reaction, no venting or  
5 condensers are required. In this way once transesterification has reached an  
6 equilibrium, the molecular weight achieved is the average of the mole content of the  
7 reactants in the beginning mixture of the second step. By first calculating the  
8 desired final molecular weight, the final weight can be achieved without further  
9 esterification which is the major time consuming step in high molecular weight  
10 polyester synthesis. Advantages of this present process are therefore lower reaction  
11 times (approximately one-half of current processes), lower waste streams, higher  
12 utilization of the commercially available condensation polymer, and higher finished  
13 molecular weights with less energy and time.

14       The process of this invention eliminates many of the problems associated  
15 with the prior art. For instance as stated in much of the prior art the digestion of  
16 PET to reconstitute the original starting materials is in many cases more expensive  
17 than the cost of manufacturing the starting materials. Once digested, the materials  
18 have to be re-condensed which is inherently energy inefficient and produces toxic  
19 levels of glycol and dioxane in the waste stream. Thus, only small amounts of PET  
20 are reprocessed in this manner. The present process eliminates these problems  
21 since it preserves the ester linkages already formed in the commercially available

1 condensation polymer so that re-condensation of precursor materials is unnecessary.

2 The high heat and duration of esterification make the manufacturing of  
3 unsaturated resins using PET, as mentioned in the prior art, a very sensitive process.

4 In many instances a polyester precursor is made first and maleic anhydride is  
5 added, reacted in, and brought up to temperatures that over time allow some  
6 isomerization of the maleic ester groups to fumaric ester groups to occur. The  
7 process described in the present application allows for the rapid transesterification of  
8 PET and isomerization of maleic groups to occur simultaneously.

#### 9 **EXAMPLE 1: WATER DISPERSIBLE POLYESTER RESINS**

10 Water soluble or dispersible resins are used in a wide variety of applications  
11 such as coatings and ink carrier vehicles. Water dispersible polyesters have become  
12 popular in recent years. These resins are solublized using a number of techniques.  
13 Generally an end group, such as a carboxylic acid, that can be subsequently  
14 neutralized is used. There are certain monomers that can also afford water  
15 dispersibility, such as sodium sulfoisophthalic acid (SIP). In the following examples  
16 we compare current techniques of reacting SIP into polyesters with the process of  
17 the present application.

18 The following example is taken from the section of preferred embodiment for  
19 US Patent 5,820,982 entitled "Sulfoaryl modified water-soluble or water-dispersible  
20 resins from polyethylene terephthalate of terephthalates" issued to Salsman in  
21 October of 1998:

1 "EXAMPLE 6

2 The following ingredients are used:

3

Ingredient	% weight	g
SIPEG (A)	30	135
Ethox 2988	5	22.5
Na-Acetate	0.5	2.25
Fascat™ 2001	0.1	0.45
PET	23.11	104
PA	41.29	185.8
Total	100%	450.00 g.

13

14

15 All ingredients except PA are charged into a reactor and heated to 205

16 degrees Centigrade. The resulting mixture is heated to 220 degrees Centigrade, then

17 cooled to 190 degrees Centigrade and tested on clear peel test. PA is charged into

18 the reactor and the mixture continued to cool down. Next day the mixture is heated

19 up to 200 degrees Centigrade for about 8 hours. When AV reaches 14.3 the mixture

20 is diluted to 30% to good particle size.

1 In this example PET is used in the reaction and broken down by the initial  
2 charge of hydroxyl-terminated materials. The SIPEG is a grade of SIP from DuPont  
3 where the sulfoisophthalic is pre-reacted with ethylene glycol resulting in two  
4 hydroxyl terminations. The PA or phthalic anhydride is used to build back the  
5 molecular weight to suitable size for film formation. The total reaction time in the  
6 flask is about 2 work days or 16 hours."

7 For comparison the same ingredients are used in present disclosure where a  
8 modifying polymer is first made and then reacted rapidly with the PET:

<u>Ingredient</u>	<u>Percent</u>	<u>Amt (in grams)</u>
Modifying Polymer		
SIPEG	30.00	63.00
Ethox 2988	5.00	10.50
Na-Acetate	0.50	1.05
Phthalic Anhydride	41.29	86.71
Fascat™ 2001	0.10	0.21
Tyzor™ TPT	0.02	0.04
Commercially Available Condensation Polymer:		
PET	<u>23.09</u>	<u>48.49</u>

1       Total                               100.00                       210.00

2

3               A small amount of Tyzor™ TPT was added at the end of the modifying  
4 polymer stage in order to insure that enough tranesterification catalyst was present  
5 for the process of this disclosure. All the ingredients were combined in a 250  
6 milliliter flask fitted with a condenser, a thermometer, a pipet for the introduction of  
7 an inert gas, an agitator, and a heating mantel with a scale controlled rheostat.

8	<u>Time</u>	<u>Temp (°C)</u>	<u>Observations</u>
9	8:16a	RT	All ingredients charged except TPT and PET,
10			80%
11	8:40a	146	Clearing, used agitation and inert blanket
12	9:00a	160	Water coming over, cut back to 45%
13	11:08a	182	Water slowing, up to 60%
14	11:31a	198	Water still slowing
15	11:50a	220	Water almost stopped, added TPT and PET,
16			80%
17	12:15p	250	All PET in, cut to 70%
18	12:30p	250	Cooled, A.V. < 5.0

19

20               In this case because the mixture contains ethylene glycol the reaction was  
21 slowed down to prevent the ethylene glycol from coming over with the water. The

1 finished resin was a clear tough solid that was readily dispersible in hot water. The  
2 total time for this process was 4 hours and 15 minutes. Much less than the 16  
3 hours of the example of US Patent 5,820,982.  
4

## 5 **EXAMPLE 2: ADHESIVE COMPOSITIONS**

6 In the manufacture of adhesives the greatly reduced cycle times become even  
7 more of an issue since the rate determining step of high molecular weights that are  
8 needed for good bond strength require long reaction times. Using the approach in  
9 the present process and even with a required slightly higher molecular weight  
10 modifying polymer a range of high equivalent ratios of hydroxyl component polymers  
11 can be made. The second step of the present process, the transesterification step,  
12 is only slightly longer (in the range of minutes instead of hours) than for lower  
13 molecular weight polymers.

14 Three hot melt adhesive compositions were prepared, two by prior art  
15 methods and one using the process disclosed in this patent application. The main  
16 purpose is to show the significant difference in processing times with the herein  
17 disclosed process over the prior art processes. A small 250 ml round bottomed  
18 flask was used in all cooks.

19 Sample 1 (Prior Art Method): All virgin raw material were used and straight  
20 esterification was performed to condense all the raw materials. The following  
21 reaction was performed.

<u>Ingredient</u>	<u>Percent</u>	<u>Amt (in grams)</u>
Peg 400	9.69	20.35
Diethylene Glycol	23.90	50.19
Trimethylol Propane	14.62	30.70
Phthalic Anhydride (PA)	46.60	97.86
Adipic Acid	5.11	10.73
Fascat™ 4100	<u>0.08</u>	<u>0.17</u>
Total	100	210.00

All the ingredients were combined in a 250 milliliter flask fitted with a condenser, a thermometer, a pipet for the introduction of an inert gas, an agitator, and a heating mantel with a scale controlled rheostat. At a later step vacuum was applied using a suitable vacuum pump with connecting hose.

Note: Fascat™ 4100 is a monobutyl stannous acid catalyst for esterifications made by Atofina™. Phthalic anhydride was used in this cook due to its lower cost and ease of reaction over terephthalic acid; however, in terms of performance for the end product application terephthalic acid is preferred.

<u>Time</u>	<u>Temp(°C)</u>	<u>Observations</u>
8:35a	RT	All ingredients charged. Heater set at 80%.
8:55a	98	Ingredients melted. Began agitation and inert blanket.
		Set Control on 44% to control reaction.

1	9:35a	160	Distillate began coming over.
2	12:05p	180	Distillate slowing down. Set control to 50%
3	1:35p	220	Set control to 60%. Began inert gas sparge.
4	3:38p	240	Began vacuum. Pulled 25 inch vacuum for one hour.
5	4:44p	240	Vacuum cut and product tested.
6	Total Cook Time: 8hrs. 9min.		

7           The product was suitably tacky and had the resilience of a higher molecular  
8 weight polymer. The Gardner Holdt Viscosity was T at 60%. The adhesion was very  
9 good.

10           Sample 2 (Prior Art Method): The process was used where some PET is  
11 broken down into oligomer segments and used to replace some of the aromatic  
12 acids. Next, the polymer is built back up using esterification. The following  
13 reaction was performed:

<u>Ingredient</u>	<u>Percent</u>	<u>Amt (in grams)</u>
14 Peg 400	9.13	19.17
16 Trimethylol Propane	30.70	64.47
17 PET pellets	45.57	95.70
18 Tyzor™ TPT	0.02	0.04
19 Terephthalic Acid	14.50	30.45
20 Fascat™ 4100	<u>0.08</u>	<u>0.17</u>
21 Total	100	210.00



All the ingredients were combined in a 250 milliliter flask fitted with a condenser, a thermometer, a pipet for the introduction of an inert gas, an agitator, and a heating mantel with a scale controlled rheostat. At a later step vacuum was applied using a suitable vacuum pump with connecting hose.

Note: Tyzor™ TPT is a Dupont tetrapropyltitanate catalyst that is known to be effective in transesterification reactions.

<u>Time</u>	<u>Temp (°C)</u>	<u>Observations</u>
8:26a	RT	Peg 400, and TMP charged. Control set at 80%.
8:50a	80	Ingredients melted. Began agitation and inert blanket.
9:41a	200	Added TPT and a third, 15 grams, of PET.
10:01a	240	Added a third, 15 grams, of PET.
10:20 a	240	Added last third, 15.57 grams, of PET.
10:43 a	250	Hold for thirty minutes at 250 Centigrade.
11:15 a	250	Turned off heat and allow to cool down.
12:30p	200	Added Terephthalic acid and Fascat™ 4100.
		Set control to 50%.
1:30p	190	Water coming over.
6:25p	220	Set up vacuum at 25 inches for 1 hour, set control at 55%.

1 7:25p 240 Finished

2 Total Cook Time: 10hrs. 59min.

3

4 Some of the additional reaction time over the first example was due to the  
5 use of terephthalic acid. If phthalic anhydride were used instead, based on previous  
6 work, the reaction should run 3 to 4 hours less.

7 The product was suitably tacky and had the resilience of a higher molecular  
8 weight polymer. The Gardner Holdt Viscosity was U+ at 60%. The adhesion was  
9 very good.

10 Sample 3 (Present Method): All other ingredients of a final polymer were reacted  
11 together to form a modifying polymer through esterification, except PET. Next,  
12 transesterification of PET was used to build molecular weight to form a final  
13 polymer.

14

15 Ingredient Percent Amt (in grams)

16

17 Modifying Polymer:

18 Peg 400 3.63 7.62

19 Diethylene Glycol 1.82 3.82

20 Trimethylol Propane 17.20 36.12

21 Adipic Acid 12.29 25.81

1	Fascat™ 4100	0.08	0.17
2	Tyzor™ TPT	0.02	0.02
3			
4	Commercially Available Condensation Polymer:		
5	PET	<u>64.96</u>	<u>136.42</u>
6	Total	100	210.00

7

8 All the ingredients were combined in a 250 milliliter flask fitted with a

9 condenser, a thermometer, a pipet for the introduction of an inert gas, an agitator,

10 and a heating mantel with a scale controlled rheostat. No vacuum step was needed

11 to increase the molecular weight.

12 Note: In this process the Fascat™ 4100 is used first for esterification of the

13 modifying polymer and then the TPT is used for transesterification of the modifying

14 polymer with the commercially available condensation polymer.

15	<u>Time</u>	<u>Temp (°C)</u>	<u>Observations</u>
16	8:29a	RT	Peg 400, DEG,TMP,adipic acid, and Fascat™
17			4100 charged, control set at 80%.
18	8:45a	90	Ingredients melted. Began agitation and inert
19			blanket.
20	9:05a	170	Condensate coming over.
21	10:10a	220	Condensate almost stopped. A.V. of less

1			than 3.0
2	10:20a	240	Added Tyzor™ TPT and first third, 45 grams,
3			of PET.
4	10:43a	250	All clear and liquid. Added second third,
5			45 grams, of PET.
6	11:03 a	250	All clear and liquid. Added last third, 46.42
7			grams, of PET.
8	11:50a	250	Held thirty minutes after reaching 250 degrees
9			Centigrade.
10			Cooled. Tyzor™ TPT added.
11	Total Cook Time:		3 hrs. 19 min.

12

13       The product was suitably tacky and had even more resilience, as indicated by

14 its recovery rate after manually stretching, than either of the two previous cooks

15 indicating an even higher molecular weight polymer than the prior samples. The

16 Gardner Holdt Viscosity was X+ at 60% again indicating a higher molecular weight

17 than either of the previous processes. The adhesion to a paper substrate was very

18 good and required more force to tear apart as evident by the large amount of fiber

19 tear observed over the previous examples.

20   **EXAMPLE 3: FILM COMPOSITIONS FROM POLYETHYLENE NAPHTHALATE (PEN)**

21       In the production of films it is essential that the viscosity, resiliency, or other

1 properties of the molten resin be high enough to hold a sheet through a drop zone  
2 when forming or laminating. With many films a certain degree of cross-link density  
3 is incorporated into the polymer to achieve this. It becomes necessary at times to  
4 approach the gelation point of the polymer in order to achieve these running  
5 properties. With the disclosed procedure one can approach the gelation point by  
6 selecting the right cross-link density in the modifying polymer achieving unheard of  
7 properties with great accuracy. In fact in many cases gelation is a necessary  
8 property to achieve high strengths and cohesive properties. With this process and  
9 the proper choice of beginning multifunctional alcohols or acids, gelation can be  
10 achieved with large quantities of the commercially available condensation polymer.

11 PEN is a relatively new polymer that has come into being in the last few  
12 years. Prior to the construction of a manufacturing site by Amoco specifically for the  
13 manufacture of NDC, or dimethyl-2,6-naphthalenedicarboxylate the intermediate for  
14 PEN, the cost was prohibitive for all but the most demanding applications. Now  
15 however many items of commerce are using PEN.

16 There are advantages of using PEN over PET for packaging of certain articles.  
17 For example the barrier properties of PET are not good enough for certain  
18 applications where barrier are necessary. PET has been used for bottling beer but  
19 because of the high permeability of oxygen it causes the flavor to deteriorate rapidly.  
20 There have been several products where PET is laminated with a high oxygen  
21 barrier film to try to compensate for this. PEN has the needed barrier properties.

This and the fact that it can take higher temperatures that are used to pasteurize some liquids, it is expected that the use of PEN will increase over the next decade.

The process of the present invention can use PEN as the commercially available condensation polymer. The required temperatures to produce this polymer are slightly greater on the order of 250 to 270 degrees Centigrade.

<u>Ingredient</u>	<u>Percent</u>	<u>Amt (in grams)</u>
Modifying Polymer		
Peg 400	53.46	112.27
Diethylene Glycol	16.28	34.19
Adipic Acid	30.11	63.23
Fascat™ 4100	0.12	0.25
Tyzor™ TPT	0.03	0.06
Total	100	210

All the ingredients were combined in a 250 milliliter flask fitted with a condenser, a thermometer, a pipet for the introduction of an inert gas, an agitator, and a heating mantel with a scale controlled rheostat.

<u>Time</u>	<u>Temp (°C)</u>	<u>Observations</u>
8:33a	RT	All above ingredients except Tyzor™ TPT, 80%
8:58a	100	All melted, agitate and inert gas

1	9:31a	170	Condensate over, set at 65%
2	11:15a	225	Condensate slowed almost to stop, A.V.<3.0,
3			removed all but 42 grams from flask, added TPT,
4			80%

5 The following combination was used for the final polymer:

6			
7	<u>Ingredient</u>	<u>Percent</u>	<u>Amt (in grams)</u>
8	Modifying Polymer	20	42
9	PEN	80	168

10

11	<u>Time</u>	<u>Temperature</u>	<u>Observations</u>
12	11:25a	250	Added 20 grams of PEN
13	11:39a	265	Cleared, added 30 grams of PEN
14	11:59a	265	Cleared, added 50 grams of PEN
15	12:33a	265	Cleared, added 68 grams of PEN
16	1:45a	265	Cleared

17

18 Finished product was a clear, stretchy material. When poured out onto a  
 19 Teflon™ sheet the material had the characteristics of the shrink wrap used in the  
 20 packaging industry. Considering the content of PEN, this film should have superior  
 21 barrier properties.

#### 1     **EXAMPLE 4: POLYESTER POLYOLS**

2             It has been shown in the prior art that PET can be broken down through  
3 glycolysis with various types of glycols to a polyol that is then further reacted with  
4 propylene or ethylene oxide to make these polyols PET-containing less crystalline  
5 and aid in the handling by lowering the viscosity of the resulting liquid. The liquid  
6 polyols are usually used to make more pliable or flexible types of finished materials  
7 such as foam for backing various substrates, foam for furniture cushions, automotive  
8 seats, etc. But there are some liquid polyols that create rigid foams as well. The  
9 need for non-crystallizing material to make polyols requires further processing with  
10 ethylene oxide or propylene oxide units to achieve the desired end product.

11            Harder more crystalline polyols can be made that are suitable for further  
12 reaction with diisocyanate prepolymers or epoxy containing polymers to make hard  
13 coatings for appliances, automotive finishes and the like that are formed by heating  
14 up or baking the polyol powder until it fuses and becomes a coating. In the process,  
15 there are many environmental aspects of having materials with low VOC's and  
16 containing no solvents that need to be removed. These are collectively referred to as  
17 powder coatings because they are normally in the form of powders ready for use.

18            In the prior art, several types of polyester polyols have been made using PET  
19 as a raw material. Polyols are useful components of a number of different  
20 compounds. These include, but are not limited to, surfactants, different types of  
21 polyurethanes from foam to thermoplastic elastomers, and adhesives or coatings.



1       The present process is especially useful for the preparation of polyols with a  
2 wide variety of properties. Furthermore, when using an extruder for the second step,  
3 the rapid transesterification step, the procedure is especially useful as a means of  
4 making and utilizing polymers of high viscosity or high crystallinity which are  
5 impossible to utilize with other manufacturing technologies that require isolation  
6 prior to use, such as high molecular weight polyurethanes. To make high molecular  
7 weight polyurethanes liquid polyols are mixed with close to stoichiometric  
8 equivalents of diisocyanate compounds and allowed to react. The isocyanate groups  
9 react with the alcohol groups of the polyols and extend the chain with the resulting  
10 urethane linkages. Due to the relatively low molecular weights of the starting  
11 polyols often the mixtures contain 30 to 50 percent of the isocyanate compound. In  
12 contrast, with the present process, it is possible to create high molecular weight  
13 polyols with wide ranges of amorphous and crystalline segments. With the polyol  
14 component at higher molecular weights, the isocyanate component can be reduced  
15 to very low levels, often less than 1% of the total.

16       Three different polyols were made using the present procedure with varying  
17 molecular weights and degrees of crystallinity. A small 250 ml round bottomed  
18 flask was used in all cooks.

19  
20 Polyol Sample 1:

21 <u>Ingredient</u>	<u>Percent</u>	<u>Amt (in grams)</u>
----------------------	----------------	-----------------------

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21

Modifying Polymer:

Peg 400	39.80	83.58
Diethylene Glycol	10.60	22.26
Adipic Acid	14.60	30.66
Fascat™ 4100	0.08	0.17
Tyzor™ TPT	0.02	0.04

Commercially Available Condensation Polymer:

PET	<u>34.90</u>	<u>73.29</u>
Total	100.00	210.00

All the ingredients were combined in a 250 milliliter flask fitted with a condenser, a thermometer, a pipet for the introduction of an inert gas, an agitator, and a heating mantel with a scale controlled rheostat. No vacuum step was used.

Note: In these examples, the Fascat™ 4100 is used first for esterification of the modifying polymer. Next, the TPT is used for transesterification of the modifying polymer with the commercially available condensation polymer of commerce.

<u>Time</u>	<u>Temp (°C)</u>	<u>Observations</u>
8:14a	RT	Peg 400, DEG, Adipic acid, and Fascat™ 4100

1			charged, control set at 80%.
2	8:35a	100	Ingredients melted. Began agitation and inert blanket.
3	9:01a	170	Condensate coming over.
4	9:15a	190	Condensate over too fast, cut back to 60%
5	10:20a	220	Condensate almost stopped. A.V. less than 5
6	10:32a	240	Added TPT and all of PET
7	10.48a	250	All clear and liquid. Clear pill of 30 minutes
8	Total Time		2 Hours and 34 minutes

9

10 The product was a clear, slightly viscous liquid at room temperature.

11 Polyol Sample 2:

12 In this example only the amounts of Peg 400 and adipic acid were changed.

13 However, this represented a change in the modifying polymer from an equivalent

14 excess of hydroxyls of .995 to .39. This shifts the molecular weight up

15 considerably, as indicated by the increase in viscosity from 15 poise at 175 degrees

16 Centigrade to 35 poise at 175 degrees Centigrade, while reducing the hydroxyl

17 content of the finished polyol.

18

19	<u>Ingredient</u>	<u>Percent</u>	<u>Amt (in grams)</u>
20	Modifying Polymer:		
21	Peg 400	34.80	73.08

1	Diethylene Glycol	10.60	22.26
2	Adipic Acid	19.60	41.16
3	Fascat™ 4100	0.08	0.17
4	Tyzor™ TPT	0.02	0.04
5			
6	Commercially Available Condensation Polymer:		
7	PET	<u>34.90</u>	<u>73.29</u>
8	Total	100.00	210.00

All the ingredients were combined in a 250 milliliter flask fitted with a condenser, a thermometer, a pipet for the introduction of an inert gas, an agitator, and a heating mantel with a scale controlled rheostat.

<u>Time</u>	<u>Temp (°C)</u>	<u>Observations</u>
12:35p	RT	Peg 400, DEG, Adipic Acid, and Fascat™ 4100 charged. Heater set at 80%.
12:55p	100	Ingredients melted. Began agitation and inert blanket.
1:26p	170	Distillate began coming over. Set heater to 60%.
3:20p	220	Condensate almost stopped. A.V. < 3.0
3:35p	230	Added all TPT and PET. Set control to 80%
4:16p	250	All clear.

1 Total Cook Time: 3hrs. 41min.

2

3 This polyol was clear and much more viscous than Polyol Sample 1. This is  
4 due to the higher molecular weight.

5

6 Polyol Sample 3:

7 In this example the same percentage of ingredients are used to make the  
8 modifying polymer as in Polyol Sample 2. However, the amount of the  
9 commercially available condensation polymer, i.e. PET, is changed so that the  
10 finished polyol contains 50%, and not 34.90% of the PET. Since the PET is of  
11 higher molecular weight than that of the modifying polymer, the molecular weight is  
12 increased substantially from the PET upon reaction with subsequent changes in  
13 properties expected of higher molecular weight polymers.

14	<u>Ingredient</u>	<u>Percent</u>	<u>Amt (in grams)</u>
15	Modifying Polymer:		
16	Peg 400	26.70	56.07 *
17	Diethylene Glycol	8.14	17.09
18	Adipic Acid	15.06	31.63
19	Fascat™ 4100	0.08	0.17
20	Tyzor™ TPT	0.02	0.04

21

Commercially Available Condensation Polymer:

PET	<u>50.00</u>	<u>105.00</u>
Total	100.00	210.00

\*Note: In order to allow the catalysts, Fascat™ 4100 and Tyzor™ TPT, to remain constant a slight adjustment was made in the quantity of Peg 400 used.

All the ingredients were combined in a 250 milliliter flask fitted with a condenser, a thermometer, a pipet for the introduction of an inert gas, an agitator, and a heating mantel with a scale controlled rheostat.

<u>Time</u>	<u>Temp (°C)</u>	<u>Observations</u>
8:21p	RT	Peg 400, DEG, Adipic Acid, and 4100 charged. Heat set at 80%.
8:40p	100	Ingredients melted. Began agitation and inert blanket.
9:08p	170	Condensate coming over, back to 60%.
10:31p	222	Condensate stopped. A.V. < 3.0, back to 80%
10:45p	250	Added 50.0 grams of PET.
11:05p	250	Added 55.0 grams of PET.
11:30p	250	Clear melt.
11:45p	250	Finished and cooled.
Total Cook Time:		3 hours 24 minutes

1  
2       At this point the product was cooled and was a tacky solid at room  
3 temperature indicative of a much higher molecular weight. Also it crystallized  
4 overnight so the crystallinity with this much PET is high. In production of high PET  
5 content urethanes as in the following examples it would not be necessary to isolate  
6 this material.

7  
8       **EXAMPLE 5: POLYESTER POLYOLS USED TO MAKE POLYURETHANES**

9       As presented in Polyol Samples 1-3, polyols are reacted with near  
10 stoichiometric amounts of diisocyanate compounds to yield polyurethanes that can  
11 be used for foam, adhesives, or other elastomeric compounds. The polyols of the  
12 present process are especially suitable to rapid modification of polyurethanes to suit  
13 a wide range of finished properties. In addition, the higher molecular weights that  
14 can be easily obtained can produce rare properties with very small amounts of  
15 diisocyanate compounds because of the higher ratio of polymer to isocyanate  
16 components the finished polyurethanes can take on properties more like the  
17 polyester and less like the isocyanates. These properties could include crystalline  
18 and non-crystalline phases within the same polymer structure resulting in a  
19 combination of properties such as rigidity and impact strength that have not been  
20 achieved with past polyurethane systems.

21       In the following examples polymethylene polyphenyl isocyanate (PAPI) was

1 used as the diisocyanate compound. It has low volatility and is therefore safer to  
2 use than standard methylene phenyl diisocyanate (MDI) one of the more common  
3 isocyanates used. The isocyanate index of PAPI 27 from Dow™ is stated to be 300.

4 This value is used to establish combining weights with other reactive groups. It is  
5 common practice to use a slight theoretical excess of isocyanate, usually 3-5% for  
6 flexible foams. Also, water is commonly used as a foaming agent in these types of  
7 mixes. The isocyanate reacts with the water creating carbon dioxide that then  
8 expands and creates the foam. The quantity of isocyanate compound used for this  
9 purpose must also be taken into account.

#### 10 Polyurethane Example 1:

11 Using Polyol Sample 1 since the equivalents of diethylene glycol and adipic  
12 acid are equal the equivalents of Peg 400 can be used to calculate the equivalents  
13 of hydroxyl components and the hydroxyl number. The hydroxyl number for this  
14 polyol is 111.6. This value is calculated by either 1) calculating the hydroxyl value  
15 of the beginning mixture and subtracting the calculated beginning acid value and  
16 then adding back the measured final acid value, or 2) using conventional techniques  
17 with anhydrides and back calculations by titration of remaining acid values.

18 Once this value is obtained, it is divided by the isocyanate index to obtain the  
19 combining ratio.

20  $111.6 \div 300 = .372 \times 100 = 37.2$  grams of PAPI per 100 grams of Polyol Sample

21  $1 + 37.2 \times 4\% = 38.7$  grams per 100



1 Using 1 gram of water for the foaming agent an amount of 14.4 grams of  
2 PAPI was added for conversion to carbon dioxide to create the foam.

3 So the following ratio amounts were combined in a cup and allow to react:

4 Polyol Sample 1 100 grams

5 PAPI 38.7 grams

6 Water 1.0 grams

7 PAPI for water 14.4 grams

8 DBTL 0.1 grams

9 The di-butyl tin laurate (DBTL) is added to help catalyze the reaction. Other  
10 catalysts such as amines are commonly used to speed up the reaction. This  
11 produced a nice foam that expanded and became slightly rigid and very tough after  
12 curing.

13 Polyurethane Example 2:

14 Using Polyol Sample 2, since the equivalents of diethylene glycol and adipic  
15 acid are equal the equivalents of Peg 400 can be used to calculate the equivalents  
16 of hydroxyl components and the hydroxyl number. The hydroxyl number for this  
17 polyol is 97.6. This value is calculated by either 1) calculating the hydroxyl value of  
18 the beginning mixture and subtracting the calculated beginning acid value and then  
19 adding back the measured final acid value, or 2) using conventional techniques with  
20 anhydrides and back calculations by titration of remaining acid values.

21  $97.6 \div 300 = .325 \times 100 = 32.5$  grams of PAPI per 100 grams of Polyol Sample 2

1     + 32.5 x 4% = 33.8 grams per 100

2             Once this value is obtained, it is divided by the isocyanate index to obtain the  
3 combining ratio.

4             Using 1 gram of water for the foaming agent an amount of 14.4 grams of  
5 PAPI was added for conversion to carbon dioxide to create the foam.

6             So the following ratio amounts were combined in a cup and allow to react:

7 Polyol Sample 2     100 grams

8 PAPI                 33.8 grams

9 Water                1.0 grams

10 PAPI for water     14.4 grams

11 DBTL                0.1 grams

12  
13             This produced a nice foam that was tough and more rigid than Polyurethane  
14 Example 1.

15 Polyurethane Example 3:

16             Using Polyol Sample 3, since the equivalents of diethylene glycol and adipic  
17 acid are equal the equivalents of Peg 400 can be used to calculate the equivalents  
18 of hydroxyl components and the hydroxyl number. The hydroxyl number for this  
19 polyol is 74.9. This value is calculated by calculating the equivalents supplied by  
20 the PEG 400. The hydroxyl number is based on the molecular weight of potassium  
21 hydroxide, which is 56.1 and is defined as being millequivalents of potassium

hydroxide per gram of sample.

Once this value is obtained, it is divided by the isocyanate index to obtain the ratio.

$$74.9 \div 300 = .25 \times 100 = 25 \text{ grams of PAPI per 100 grams of Polyol Sample 3} + \\ 25 \times 4\% = 26 \text{ grams per 100}$$

Using 1 gram of water for the foaming agent an amount of 14.4 grams of PAPI was added for conversion to carbon dioxide to create the foam.

So the following ratio amounts were combined in a cup and allow to react:

Polyol Sample 3	100 grams
PAPI	26 grams
Water	.82 grams
PAPI for water	8.5 grams
DBTL	0.1 grams

In this example less water is used because the total amount of sample is less. Because the polyol of this example was a solid at room temperature it was necessary to first warm it in order to melt it to a liquid form before adding all of the ingredients. This produced dense cell structured foam that expanded and became very rigid and tough after curing.

In all of the above polyurethane examples, foam was generated by mixing liquids at temperatures close to room temperature. It is easy to see that the trend is

as the hydroxyl content is lowered, the molecular weight goes up, and the amount of PAPI required to produce a foam is less. However we rapidly approach the point where the polyol becomes a solid and cannot be reacted easily with the isocyanate in a cup or mixing container. The next examples are performed in an extruder.

#### Polyurethane Example 4

In this example the modifying polymer is prepared and then reacted with the PET in the same reactor. The resulting product is then transferred to an extruder where it is reacted to make the polyurethane. PAPI is injected in a zone downstream from the feed throat. Because of the high temperatures, reaction takes place rapidly and as the polymer exits it expands as foam. The raw materials of the modifying polymer in this example have been changed to reflect the diversity of alcohols and acids that can be used.

#### Modifying Polymer:

<u>Ingredient</u>	<u>Amount</u>	<u>Actual Percent</u>
Peg 600	52.20	56.80
Peg 200	20.00	21.76
Phthalic Anhydride	19.60	21.33
Fascat™ 4100	0.08	0.09
Tyzor™ TPT	<u>0.02</u>	<u>0.02</u>
Total	91.9	100.00

Reaction with PET:

<u>Ingredient</u>	<u>Percent</u>
Modifying Polymer	19.6
PET	78.4
5-Phenyl Tetrazole	2.0

In this example the modifying polymer was prepared in advance in a small reactor. PET was later added in stages and the reaction was heated to 250 degrees Centigrade until no change in viscosity was noticed. The resulting material was cooled to about 100 degrees Centigrade and the 5-phenyl tetrazole was added. This is a common foaming agent used in high temperature polymers. However, since extremely high temperatures are not needed, other suitable foaming agents will work such as, but not limited to, hydrocarbons, such as hexane or heptane, inert gases such as nitrogen, carbon dioxide, or any of the noble gases.

At this point the polyol polymer was transferred to a twin screw extruder using a Nordstrom™ hot melt pump. The processing temperatures had to be high enough at the end to effect the decomposition of the 5-phenyl tetrazole to nitrogen gas in the range of 230 to 265C. PAPI was injected into the polyol polymer at about 100 degrees Centigrade and the barrel was brought up to 250 degrees Centigrade to effect decomposition of the 5PT prior to exiting the dye. The following

ratios of polyol polymer to PAPI were used:

<u>Ingredient</u>	<u>Parts</u>	<u>Percent</u>
Polyol polymer from above	100	90.58
PAPI (Stoichiometric plus 4%)	<u>10.4</u>	<u>9.42</u>
Total	110.4	100.00

The foam created was very rigid and tough and suitable as structural foam.

#### Polyurethane Example 5:

In this example the modifying polymer was added with the PET in a twin screw extruder and the transesterification reaction was performed in the barrel of the extruder. PAPI was reacted in a further downstream injection and the subsequent foam was generated with a hydrocarbon gas former. This example shows the lower quantities of isocyanate that can be used with higher molecular weights.

<u>Ingredient</u>	<u>Parts</u>	<u>Percent</u>
PET	100.00	95.90
Modifying Polymer of Polyol Sample 2	1.50	1.44
PAPI	0.78	0.74
Heptane	<u>2.00</u>	<u>1.92</u>

Total	104.28	100.00
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The foam created was extremely rigid and tough and suitable for many kinds of structural uses.

It is in the actual comparison of reaction rates and times for the present process that one becomes aware of the novelty in the present process since the present process is not only faster but much easier to control than those of the prior art. Another substantial benefit of the present process relates to the time for research and development of new polymer types. Instead of being limited to only the beginning mixture of ingredients one can vary the commercially available condensation polymer ratio in the second step of the process and extract research samples along the way thereby producing a wide range of polymer species for property comparisons.

Although the invention has been described with reference to specific embodiments, this description is not meant to be construed in a limited sense. Various modifications of the disclosed embodiments, as well as alternative embodiments of the inventions will become apparent to persons skilled in the art upon the reference to the description of the invention. It is, therefore, contemplated that the appended claims will cover such modifications that fall within the scope of the invention.

